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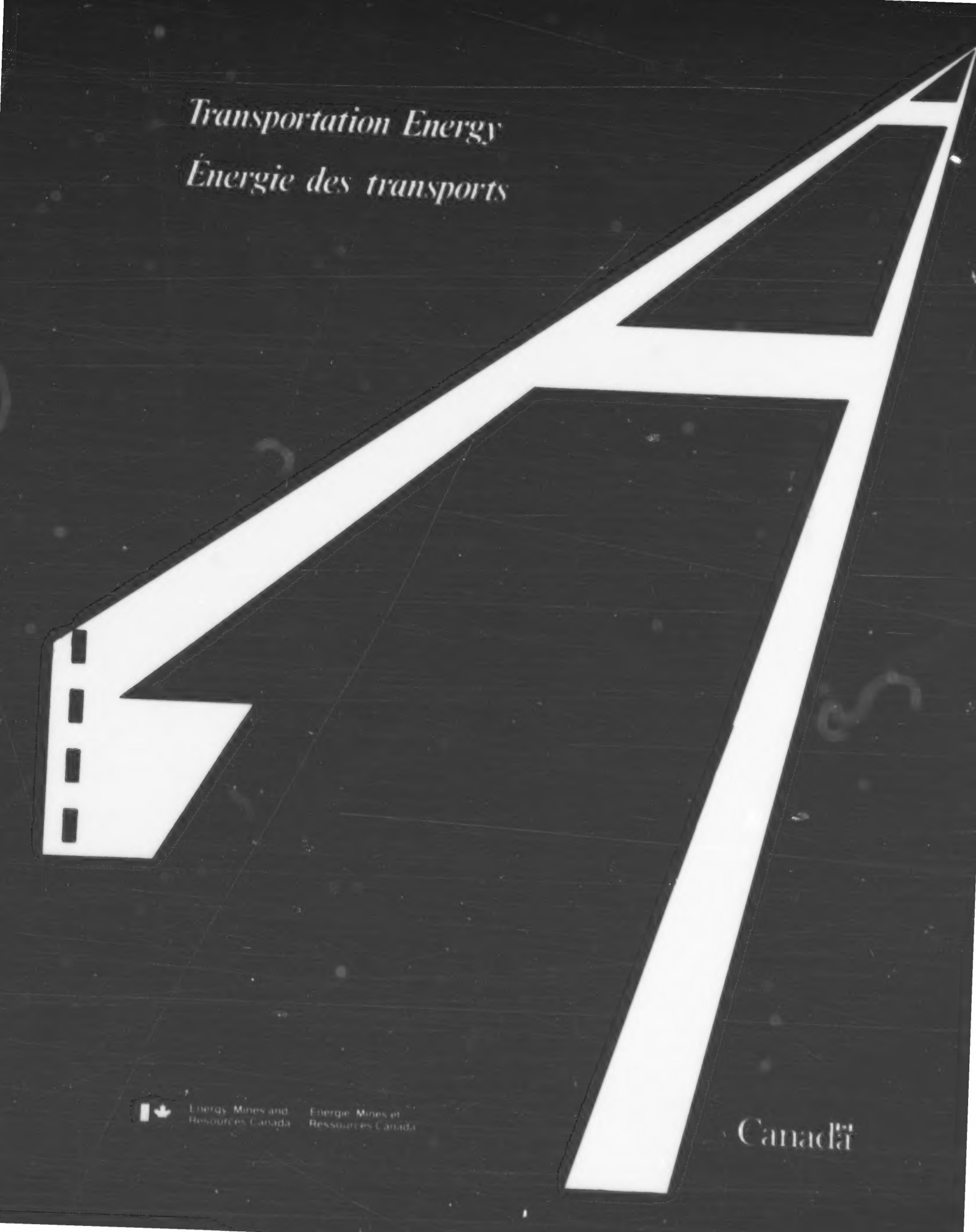

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REID VAPOUR PRESSURE OF BLENDS OF COMMERCIAL GASOLINE AND ALCOHOLS

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DISCLAIMER

This study was carried out with the cooperation of the Department of Energy, Mines and Resources. However, the views expressed in the report are those of the author and do not necessarily reflect the views of the Department.

TABLE OF CONTENTS

		PAGE
1.	Introduction	2
2.	Sampling and Blending Procedure	3
3.	Vapour Pressure Testing	4
4.	Water Content of Base Fuels	8
5.	Analysis by Gas Chromatography	9
6.	Conclusions	9

Summary

Blends of gasoline and low molecular weight alcohols (methanol, ethanol, propanols, and butanols) are currently marketed in a number of areas of Canada. These blended fuels do not always meet the requirements of the applicable Canadian General Standards Board (CGSB) standard due to the significant Reid Vapour Pressure (RVP) increase which results from the alcohol addition.

In order to assess this vapour pressure increase ten samples of commercial gasolines were obtained in the Ottawa area and RVP was determined on the samples as received and in blends with alcohols. The results are presented which indicate the magnitude of the RVP increase with alcohol addition.

Some recent work has indicated a difference in the gasoline alcohol blends RVP vis temperature relationships compared to straight gasoline RVP vs temperature. Limited testing was done of this effect of temperature on RVP for a straight gasoline and a blend of gasoline with methanol and a cosolvent alcohol.

Résumé

Les mélanges de gazoline et d'alcools à faible masse moléculaire (méthanol, éthanol et butanols) sont présentement offerts sur le marché dans plusieurs régions du Canada. Ces mélanges ne satisfont pas toujours les normes applicables émises par l'Office Canadien des normes générales, due à l'augmentation significative de la tension de vapeur Reid (TVR), résultant de l'addition d'alcool.

Afin d'estimer l'augmentation de la tension de vapeur un échantillon de dix gazolines commerciales a été prélevé dans la région d'Ottawa. La TVR a été déterminé pour les échantillons reçus ainsi qu'une fois mélanger avec des alcools. Les résultats présentés indique la magnitude de l'augmentation de la TVR lorsque de l'alcool est mélangé à la gazoline.

Certains travaux récent indiquent une différence dans la relation TVR et température lorsque la gasoline contient de l'alcool. Des essais limité ont été fait sur cette relation TVR et température sur de la gasoline contenant du méthanol et un alcool comme cosolvent.

Reid Vapour Pressure of Blends of Commercial Gasoline and Alcohols

1. INTRODUCTION

The success of gasoline/alcohol blends as automotive fuels depends upon the simplicity of production as it affect the economics of the fuel produced. From this point of view, it would be desirable to produce gasoline/alcohol blends by adding the alcohols to finished gasolines and so avoid the complexity and added cost of producing a specially tailored gasoline base.

A blend made this way poses a problem in terms of quality. The principal concern is related to the increase in Reid Vapour Pressure caused by the added alcohol. With the trend toward higher vapour pressure gasolines, there is a significant danger that gasolines in the higher volatility classes would be driven over the specification limit of 97 kPa by the addition of the percentages of alcohols considered in this investigation. Such a high vapour pressure fuel could lead to drivability problems and difficult hot starting in many vehicles due to vapour lock. Additionally, there has been speculation that the vapour pressure versus temperature behaviour of gasoline/alcohol blends differs significantly from that of typically available commercial gasolines. Blends that exceed the RVP specification limit at 37.8°C may not be sufficiently volatile to permit easy starting at low (winter) temperatures.

To investigate this concern a test programme was developed using finished gasoline in three typical blends with alcohol; one with ethanol only and two with methanol and cosolvents. The blends used are currently considered as likely commercial possibilities. Testing was divided into two phases, the first dealing with standard testing to determine conformity with established specifications, and the second an attempt to determine how the vapour pressure vs. temperature behaviour of alcohol blends differs from that of straight gasoline.

For this programme, ten samples of winter grade regular unleaded gasoline were obtained locally at filling stations. Each of these samples was tested for RVP as obtained and in the three alcohol/gasoline blends, namely 10% ethanol, 5% methanol with 3% ethanol, and 5% methanol with 3% tertiary butyl alcohol cosolvent (TBA). The results are detailed in Table 2. As well, the base gasoline was tested for water content by Karl Fischer and GC analysis was performed to confirm that there was evidence of any alcohols present in the gasolines as received.

Two samples wre then chosen (2A and 2C) representing a straight gasoline and a methanol/cosolvent/gasoline blend and vapour pressure was determined on each sample at three different temperatures. A graphical representation of this data is presented in Graph 1.

2. SAMPLING AND BLENDING PROCEDURE

Samples were collected in one gallon plastic safety cans directly from the pump nozzles at the filling stations. Before use, these cans were rinsed with petroleum ether and air dried. Approximately five litres of unleaded regular gasoline was purchased at each of ten gas stations around Ottawa; these are coded in the table below:

TABLE 1: IDENTIFICATION OF SAMPLES

CAN #	GAS STATION
1.	Brand Name Supplier
2.	Local Distributer
3.	Brand Name Supplier
4.	Local Distributer
5.	Local Distributer
6.	Local Distributer
7.	Brand Name Supplier
8.	Brand Name Supplier
9.	Local Distributer
10.	Brand Name Supplier

The samples were collected in a two hour period on the morning of March 14. The temperature was -2°C.

The samples taken at the gas stations are identified by the numbers given in the table. Each of these samples yielded four one litre cans of blends for testing, which are identified by the sample number and the letter A, B, C or D, according to the following scheme, which indicates fuel constituents by volume:

A Base fuel unblended
B 10% ethanol, 90% base fuel
C 5% methanol, 3% ethanol, 92% base fuel
D 5% methanol, 3% TBA, 92% base fuel

For blending, 40 one litre cans were prepared. Blending was done on the basis of one litre quantities. For example, for a blend of 10% ethanol, 100 ml of ethanol was added to the can by pipette, followed by 900 ml of gasoline measured in a 1000 ml graduated cylinder. In the case of unblended base fuel samples (label A), the one litre cans were filled to approximately 80% capacity directly from the plastic sample cans. All samples were stored at 5°C and were removed only briefly for blending in order to eliminate loss of light ends as much as possible. The alcohols were stored cold, except TBA which freezes at 25°C.

The prepared cans were placed in the cold (0°C) refrigerator in preparation for RVP determinations. Before proceeding with the measurement of RVP, approximately 200 ml was discarded from the cans containing blended fuel, leaving them 80% full as stipulated in the test method (ASTM D323).

3. VAPOUR PRESSURE TESTING

A single determination of the Reid Vapour Pressure was made for each sample by ASTM D323. In accordance with suggestions given in the Information Document on Gasohol in the 1985 Annual Book of ASTM Standards (vol. 5.01), the following modifications to method D323 were made to protect the samples from exposure to water:

- all components of the apparatus were rinsed with acetone and air dried before each test.

- the gasoline and air chambers were plugged with rubber stoppers as soon as they were dry.

- the gasoline chamber and the sample transfer tube were chilled in the 0°C refrigerator (as opposed to a bath).

- the air chamber was wiped dry quickly before the stopper was removed.

Method D323 with these modifications is usually called the Dry Method for RVP.

Table 2 lists Reid Vapour Pressure in kPa (absolute) for all samples, and the deviation from (increment to) the base fuel RVP for all gasoline/alcohol blends. The averages for RVP and the deviations are included at the bottom for each blend composition.

Note on RVP Specification

The Canadian Government Specifications Board (CGSB) standard for unleaded gasoline (CAN 2-3.5M79) specifies that in the period from 1 March to 30 April the Reid Vapour Pressure of unleaded gasoline shall not exceed 97 kPa. However, in the period immediately preceding, from 1 November to 28 February, the maximum allowable RVP is 103 kPa. It is practical, both for petroleum refiners and gasoline users, that the vapourpressure of gasoline being produced be adjusted gradually in accordance with the seasons. The effect of this practice and of residual high vapour pressure gasoline in the filling station reservoirs may have worked in combination, with the result that three of the base gasolines purchased exceeded the RVP specification in effect on March 14, the date of purchase.

It must be remembered that the 'dry method' was used for RVP determinations. While this method seems to have popular acceptance for fuels containing alcohols, it is not exactly the method required by the specification.

TABLE 2: REID VAPOUR PRESSURE (kPa)

Base Gasoline #	Blend A	Blend B	Blend C	Blend D
1	98.60	105.35	116.25	115.42
		6.75	17.65	16.82
2	97.29	103.42	113.90	113.35
		6.35	16.61	16.06
3	97.97	104.32	115.21	114.18
		6.35	17.24	16.21
4	96.66	102.18	113.63	113.07
		5.52	16.97	16.41
5	94.87	100.87	109.08	111.49
		6.00	14.21	16.62
6	86.94	93.22	103.97	102.46
		6.28	17.03	15.51
7	96.53	103.63	114.73	113.69
		7.10	18.20	17.16
8	95.29	101.15	112.04	111.35
		5.86	16.75	16.06
9	95.70	100.59	111.70	111.56
		4.89	16.00	15.86
10	96.25	100.94	112.32	111.83
		4.69	16.07	15.58
Average	95.63	101.56	112.25	111.83
		5.93	16.62	16.20

The number listed under each vapour pressure in columns B, C, and D is the increase in that vapour pressure over the base fuel RVP. Because of the possibility that the incremental vapour pressure due to the addition of alcohols depends upon the vapour pressure of the base fuel, the average was recalculated excluding fuel #6. All the fuels except #6 (RVP of 86.9 kPa) had a nominal RVP of 97 kPa (14 psi).

	Blend A	Blend B	Blend C	Blend D
New Average	96.53	102.46	113.14	112.87
		5.93	16.61	16.34

These results are not significantly different from the averages based on all the fuels which indicates that over the RVP range of the fuels listed, the effect of base RVP increase is not significant.

4. WATER CONTENT OF BASE FUELS

Each of the base fuel samples was tested for water content by D 1744 with the automatic Karl Fischer apparatus. Samples were drawn with a glass syringe directly from the cans which had been used for the vapour pressure determinations. All determinations were repeated once, and, in the case of significant disagreement between the first two results, were done a third time.

The following table lists the results in parts per million (ppm).

Fuel #	First	Second	Average
1	64	67	66
2	58	60	59
3	69	75	72
4	66	61	64
5	120	102	111
6	69	74	72
7	74	80	77
8	62	69	66
9	62	68	65
10	43	54	48

5. ANALYSIS BY GAS CHROMATOGRAPHY

After completion of the vapour pressure and water content test programs, all the base fuel samples were analysed by gas chromatography. This analysis was motivated by some recent speculations that alcohol containing fuels were being sold locally as gasoline. Inspection of the GC profiles revealed no evidence of any oxygenates in any of the fuels. This result was anticipated because of the consistency of the Reid Vapour Pressure results.

As a check, one of the blended fuels (7C) containing methanol and ethanol was chosen at random and analysed by GC for alcohol content. Calculation of the volume percentages of alcohols present yielded 4.9% methanol and 3.0% ethanol. The original blend had been mixed with 5% methanol and 3% ethanol; these results are considered to be within the tolerances for mixing and subsequent measurement of the constituents.

6. CONCLUSIONS

Adding methanol or ethanol to a gasoline increases its vapour pressure substantially; the feasability of adding alcohols to finished (commercial) gasolines is largely dependent on the tolerable increase in vapour pressure. The most important part of the results of this investigation is the determination of the increases in vapour pressure expected upon addition of the specified quantities of alcohols to gasoline. For the unleaded regular winter grade fuel used in this programme, the anticipated increase is on the order of 6 kPa (1 psi) for the 10% ethanol blend and 16 kPa (2 1/2 psi) for the methanol/cosolvent blends. Since the base gasolines had Reid Vapour Pressures in the 96 kPa range, the addition of these percentages of alcohol would bring the blend RVP's close to or above the specified maximum limit of 97 kPa (14 psi), rendering most of them above the specificatons limit.

The mechanism behind the increase in vapour pressure is complex, and there is no straighforward correlation between the amount of alcohol added to a gasoline and its resultant vapour pressure. When light alcohols are added to gasoline in small quantities, i.e. less than 15%,

the effect of the interaction between alcohol and gasoline on the molecular level is a far more significant influence on the final vapour pressure than is the vapour pressure of the neat alcohol. For this reason, these results can be taken as valid only for specific blends tested; slightly different compositions could have substantially different characteristics.

The gasolines obtained for this program were acceptably dry and contained no oxygenates. One fuel (#5) did contain more water than the others, but it is conceivable that this was due to water on the filler nozzle (rain or snow).

As can be seen in Graph 1 the change in vapour pressure versus temperature is different for a blended fuel than for a straight gasoline. At the usual test temperature of 38°C there is a large difference in vapour pressure but as the temperature is reduced to 0°C the difference in results is very small. It has been reported by others (1) that the two lines may cross so that low temperature the alcohol blend will have a lower vapour pressure that straight gasoline. This could result in difficult cold starts on alcohol blended fuels.

RVP Vs TEMPERATURE